

Sulfonylimide Ionelastomer Heterojunctions

Hayward Laboratory - University of Colorado Boulder
Joshua Sharpes

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Abstract

Polyanion(EA)/Polycation(AT) heterojunctions are materials which have potential to be used as conductors under unique circumstances due to the unique property of using ions for conductance rather than electrons. This research characterizes these junctions in accordance with this potential by exploring trends revealed by electrical characterization in materials, optimized for sustainable performance. An independent variable of the amount of ions is altered to yield properties such as threshold voltages and rectification ratios through cyclic voltammetry testing of 2 cycles from -1 to +1 volts. Through altering the condition and performing multiple tests, the sustainability of these materials are analyzed for the given magnitude range.

1. Background and Objective

Junction diodes can be thought of as synonymous to semiconductor junctions used in solar panel applications in that charge is uniformly carried across the material. The distinction between semiconductor and ionic diodes is that semiconductor diodes carry electrons which are relatively massless while ionic diodes carry free ions which have significant mass. Mass in this context is inversely correlated with potential differences of these materials due to the need for the charge carrier to diffuse through its fixed environment. Semiconductor diodes thus have substantially higher voltage drops than ionic diodes and thus different applications. If a potential difference across a material is substantial enough, ion generation in that material will occur since molecules, often part of the fixed environment, will break apart into ions. This is commonly referred to as electrochemistry and such behavior was avoided in these experiments by using lower voltages (+1 V Max) such that ion flow with a fixed number of ions between the junctions was analyzed.

Previous research has been conducted by Hyeong Jun Kim [1] of the Hayward Group to characterize the ionic diodes capacitive and resistive properties. The assumption carried throughout this research was that the interface connecting the junctions was uniform in composition similar to a semiconductor junction setup in that there was a sharp distinction between the junction layers at the ionic double layer (IDL) interface. This distinction would be due to uniform bonding of network components between chains across the IDL that would resemble polymer crystallinity (Figure 1.1):

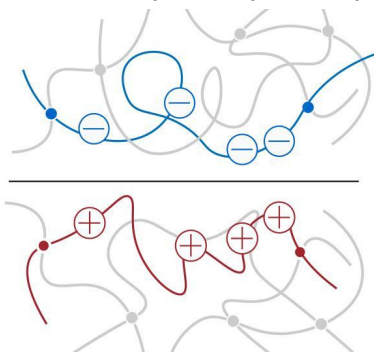


Figure 1.1: IDL interface diagram of previously perceived parallel chain orientation

This theory was brought into question by results that suggested that there was a contrasting material composition at the diode [Figure 1.1]. These results, obtained through mechanical strain testing, revealed that a substantial increase in ion flow resulted from lateral stretching which is counterintuitive to the semiconductor notion because ion flow was only expected to slightly increase. These results suggested that a breakage of some sort of material buffer residing at the IDL allowed for a temporary burst in ion flow (noted by spikes in part B of Figure 1.2).

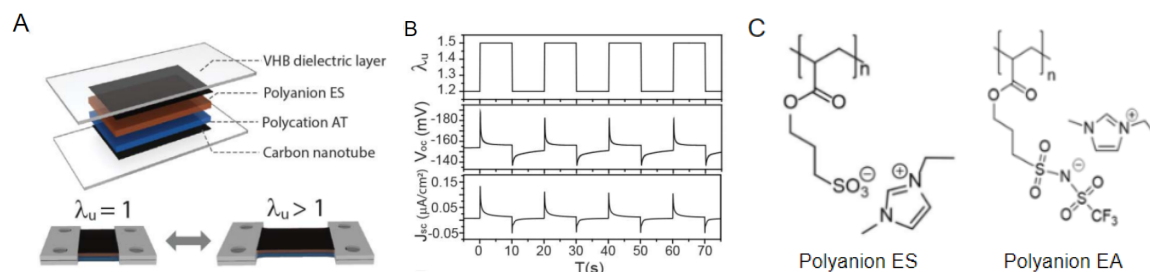


Figure 1.2: (A) ES-AT strain testing Setup, (B) Upper Graph: Strain Cycles, Middle Graph: Resulting Voltages, (C) Old (ES) and new (EA) polyanions.

The polymers used to assemble the heterojunction in Figure 1.2 are slightly different for the ones used in this research as while the polycation is the same, the polyanion is different. ES (Table 2.1 for chemical information) is a substance that is significantly hygroscopic such that experiments had to be performed within a desiccator so that ambient conditions could be replicated. Since this research was performed, methods have been developed to synthesize a similar compound, EA, that is not hygroscopic making testing applications drastically more accessible. The results in part B of Figure 1.2 suggest that there is not merely uniform ion pairing between the fixed network substituents but rather the presence of free counterions that are breaking up these original interfacial bonds.

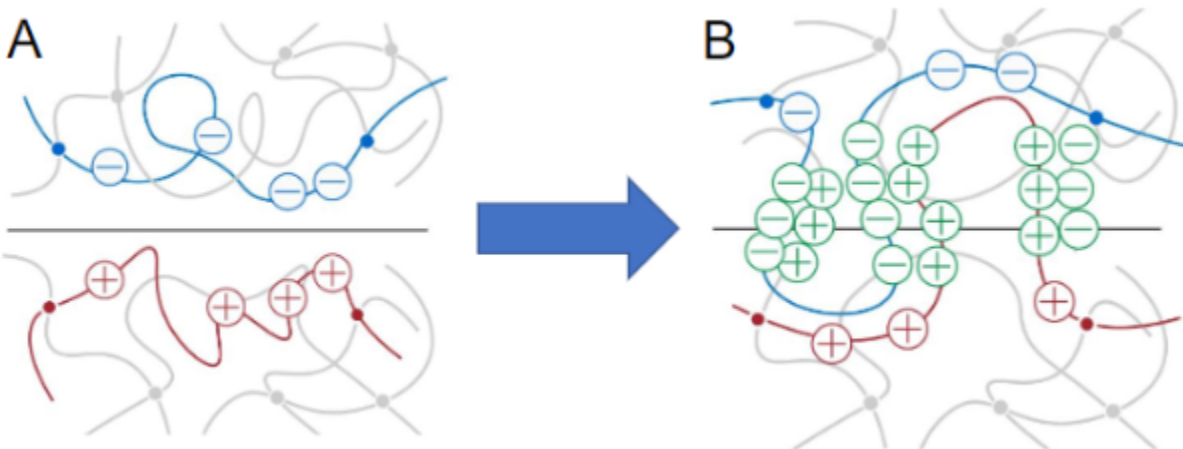


Figure 1.3: (A) Original perception of IDL interface, vs (B) Hypothesized (evolved) perception of IDL interface

The presence of counterions in the interface would result in swelling of polymer chains and thus more free volume. The amount of free volume is presumably proportional to the current of the

material for fixed parameters since more ions would be able to flow through an area with less steric hindrances. This relationship gives key insight as to how the free counterions are distributed throughout the material at a given point in its after movement due to potential difference and subsequent indications about the lack of movement, that is accumulation. There is an expected hysteresis nature of the materials such that free ions will accumulate at either one of the two sides of the interface (polycation/anion) or at the interface itself. Since the initial breakage of the IDL will accelerate ion flow and thus the current, it is expected that an initial acceleration of ions across the IDL will succeed the threshold voltage point, reflected by the I-V curves in the forward bias region. Since only a limited amount of ions are in the material (no generation), ion flow was expected to diminish with an increasing number of cycles. With less ions flowing, that is more accumulating on respective sides of the junctions, the potential difference across the diode required to break the IDL was expected to increase and the maximum current, that is the current at the maximum voltage, was expected to decrease. This hypothetical trend is demonstrated in the following figure (1.4):

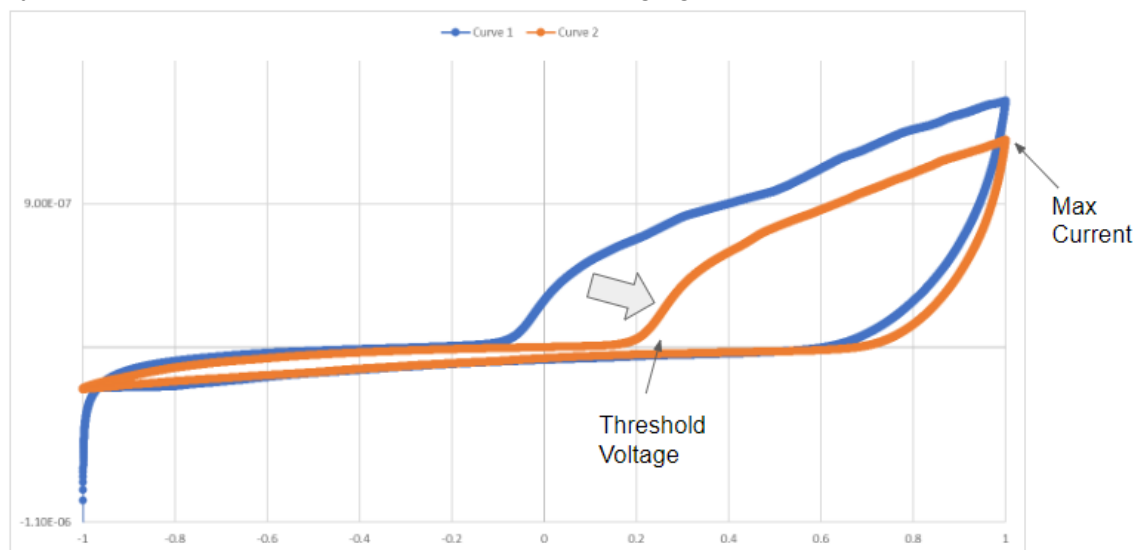


Figure 1.4: Expected current vs voltage diagram voltage cycle shift showing increasing threshold voltage and decreasing maximum current.

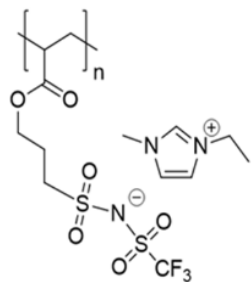
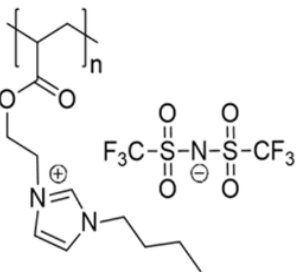
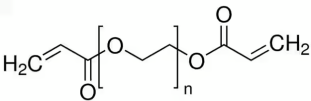
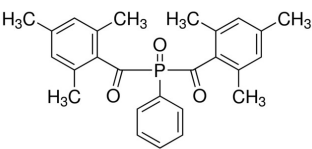
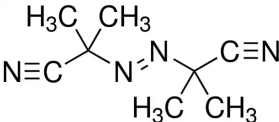
From these predicted trends, it was decided that the threshold voltage and the max current changes should be observed and measured for each of these tests. This would give insight as to how the initial hysteresis occurs under each condition measured. The initial hysteresis is most significant with these cycles (curves) as the change is asymptotic over the cycles.

Experiments were performed to investigate the mysterious behavior of these ionic diode IDLs from Jun Kim's research through testing of heterojunction electric properties. There are two potential applications that can be derived from these findings: the use of polymeric diodes and flexible adhesives [2]. Because of the hysteresis mentioned, methods have been proposed towards changing the junction orientation, such as implementing a sandwich-like junction set up polyanions around a polycation, to potentially reduce this hysteresis. The hysteresis that is encountered in these findings indicates the behavior of the junction over multiple cycles which has a more direct application in yielding characterization of the IDL for adhesion purposes. That

is, through characterizing the electrical behavior of these materials, projections can be made on how these materials interact with other materials and bind on to them in different conditions. Scenarios in which materials must endure conduction but continuously adhere to a different material will have a range of their limitations which can be established from findings in this research and research alike.

2. Materials

Table 2.1: Chemical Species

Chemical Name	Molecular Formula	Name	Molecular Structure	Notes
1-Ethyl-3-methylimidazolium tetrafluoroborate		EA		Polyanion, also known as [EMIM] ⁺ [APST] ⁻
(1-acryloyloxypropyl)-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide		AT		Polycation, also known as [AEBI] ⁺ [TSFI] ⁻
Polyethylene Glycol Diacrylate	C ₈ H ₁₀ O ₄	PEGDA		Crosslinker, 250 g/mol
Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	[(CH ₃) ₃ C ₆ H ₂ CO] ₂ P(O)C ₆ H ₅	819		Photoinitiator
Azobisisobutyronitrile	C ₈ H ₁₂ N ₄	AIBN		Thermal Initiator

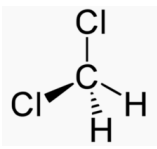
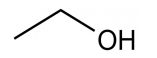
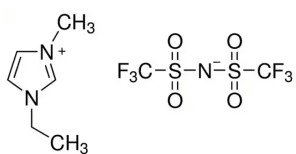
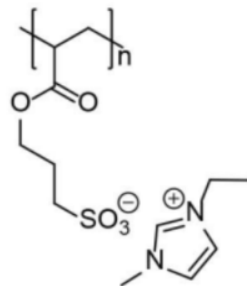
Methylene Chloride	CH_2Cl_2	DCM		Solvent for photo-polymerized resin and washing agent for junctions
Ethanol	$\text{C}_2\text{H}_6\text{O}$	EtOH		Solvent for thermally polymerized resin
1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	$\text{C}_8\text{H}_{11}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$	IL		Ionic Liquid (salt) that is added in varying amounts to junctions - source of free ions
1-ethyl-3-methylimidazolium (3-sulfopropyl)acrylate		ES		Polyanion used in previous research

Table 2.2: Lab Materials

Material	Function
Carbon Cloth Electrodes	Hoist resin junctions and allow for conduction devices, tape, to be applied
Gamry Instruments Framework - Hardware and Software	Hardware applied voltage to junctions and software display resulting current along inputted voltage
Conductive Copper Tape	Transient material for voltage application to junctions through contact with electrodes
250 μm Paper	Used to controls thickness individual resins upon assembly through glass slides
Glass Slides	Used to hoist resin photo-polymerization
VHB Tape	Used to insulate the junction setup from an disturbances for voltage cycle testing

UV Nail Dryer	Used as a light source for photopolymerizations
Hot Plate	Used as heat source for thermal polymerizations
Nitrogen Gas	Used as inert blanket gas for thermal polymerizations to remove oxygen
Binder Clips	Used to hold glass slides together with junction setup for photo-polymerization

3. Methods

A device had to be assembled that connected the two polymers, polycation EA ([EMIM]⁺[APST]⁻) and polyanion AT ({AEBI}⁺[TSFI]⁻) such that a surface area of contact (interface) could be measured. Identical surface areas and thicknesses were selected for this experiment to produce comparable samples. Furthermore, electrical wiring for conductance measurement needed a medium to connect to the polymers as the polymers had noticeably stickiness, so a carbon electrode was implemented on both sides of this heterojunction. To avoid capacitance/resistance effects of the electrode itself in measuring the conductance, the electrode had to be absorbed with the same material it was measuring which is a facet of the carbon nanotube electrode that distinguished itself from traditional electrodes for the purpose of this experiment. These carbon cloth electrodes were shown to have similar absorption properties of the ionic liquid being used in comparison to the polymers themselves.

3.1 Electrode Polymerization (Setup: Outside Layers)

To integrate these polymers into these electrodes, the liquid-resin monomers had to be polymerized by means of heat rather than light since light was not accessible through these electrodes to the extent that the entirety of the resin could be feasibly polymerized. Polymer resins were prepared through the combination and mixing of monomers (EA or AT), crosslinker (PEGDA), and initiator (AIBN). The mixing had to occur in the presence of a solvent as the components were scarce enough in density to where steric hindrances would not allow for a truly uniform mixture. Thermal polymerizations of the resins were performed through use of a thermal initiator in lesser concentration than the photo initiator (819) due to the availability of higher temperatures. The crosslinker mole-percent was kept constant between the light and heat methods as its contributions were deemed method-independent due to the same substance being used for both methods. The thermal polymerizations were carried out on a hotplate at sufficient temperatures such that the ethanol solvent used to hoist the liquid resin, crosslinker, and initiator was boiled off at about 80 °C before the polymerization reaction took place on the 130 °C surface. This reaction had to take place in the absence of oxygen due to oxygen's ability to terminate growing chains and so such elimination was implemented by the use of a nitrogen gas blanket which pushed oxygen away as the reaction proceeded. The reaction reached optimal completion, that is before diminishing conversion, at about one hour

after initiation. Carbon electrode samples containing polymerized resin were collected and used to set up the internal layers of the heterojunctions.

3.2 Resin Polymerization (Setup: Inside Layers)

There were less steps involved in setting up the inside layers of the heterojunctions as these did not need to be hosted within a material such as an electrode. Thus the polymerizations were powered by a light source which required a photo initiator (819) in the presence of the crosslinker and monomers. Both initiators were large in size (Table 2.1) and so solvent had to be used to mix all the components together for composition uniformity and this solvent had to be removed by means of mechanical force and was done so overnight through an available vacuum. With the solvent removed, the resins were molded upon a carbon electrode from the previous step containing the matching polymer (EA or AT). This molding process required geometrical control of the region in which the resin could mold, which was implemented through the use of 250 μ m paper-spacers. Glass slides that were transparent enough for light transmission from an outside source were used on either side of the electrodes to encapsulate the spacers and electrodes for the intended rectangular geometry. These glass slides were held together with binder clips as these clips provided adequate but not excessive pressure to hold the materials together. These glass slides had to be ionized so that the resin, before and after polymerization, was not not able to stick to slides and could be removed from the slides for further processing. This ionization was performed with a fluorinating agent after cleaning steps were implemented.

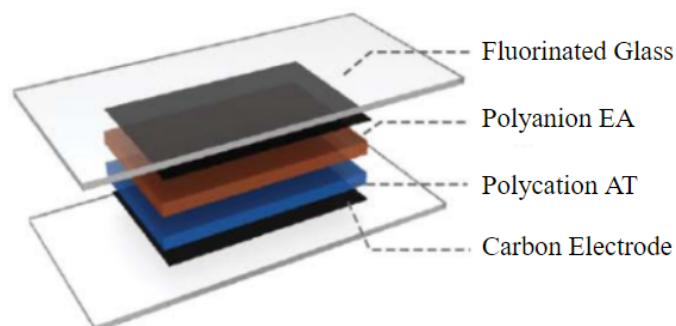


Figure 3.2.1: Heterojunction setup for photo-polymerization step

Once the resins covered the entirety of the intended electrode area, the polymerizations were performed with low-wavelength light (360-390 nm) provided by a UV nail polish dryer (Table 2.1). With this wavelength range, light source was provided towards the resin for 30 minutes per sample. Next, the polymerized samples were cut into 0.5x0.5 cm surface areas. These cut samples were then washed with a volatile solvent, Dichloromethane (DCM), which removed all of the unreacted monomer for a more refined sample.

3.3 Heterojunction Assembly

A heterojunction was assembled by combining a polyanion and polycation monolayer together such that the resins of both samples were in contact, as shown below in Figure 3.3.1:

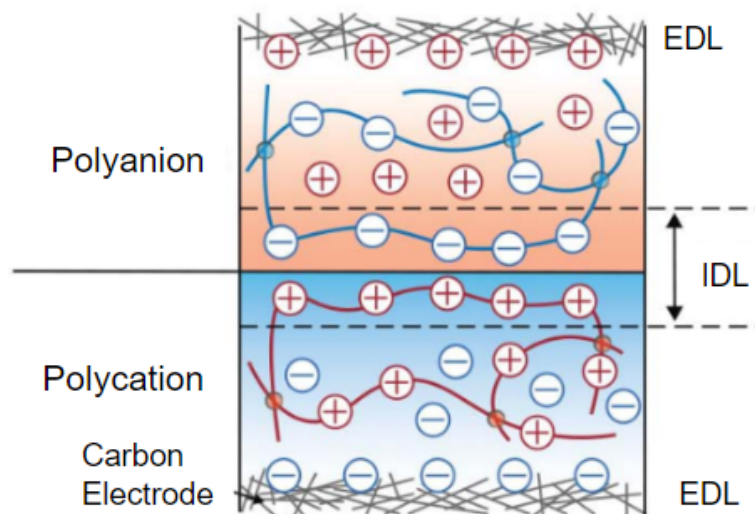


Figure 3.3.1: Heterojunction consisting of EA EDL (Top), AT EDL (Bottom), and Connecting Ionic Double Layer (Middle)

Once combined, the heterojunction samples were washed with DCH again, this time to remove the freemoving counterions from the interface of the sample so that the amount of ions in the region of interest for each sample were essentially tarred to zero. Having charge-neutral compounds on molecular level, a predetermined amount of ionic liquid (1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) was added to each sample in presence of solvent to absorb into the sample over the following two days. The amount of ions that actually absorbed into the sample was not determined from these samples directly but rather through characterizing partitioning behavior from the result of conductivity measurements (Section 3.5). Listed below is a schematic that shows the entirety of the samples setup up to this point (Figure 3.3.2):

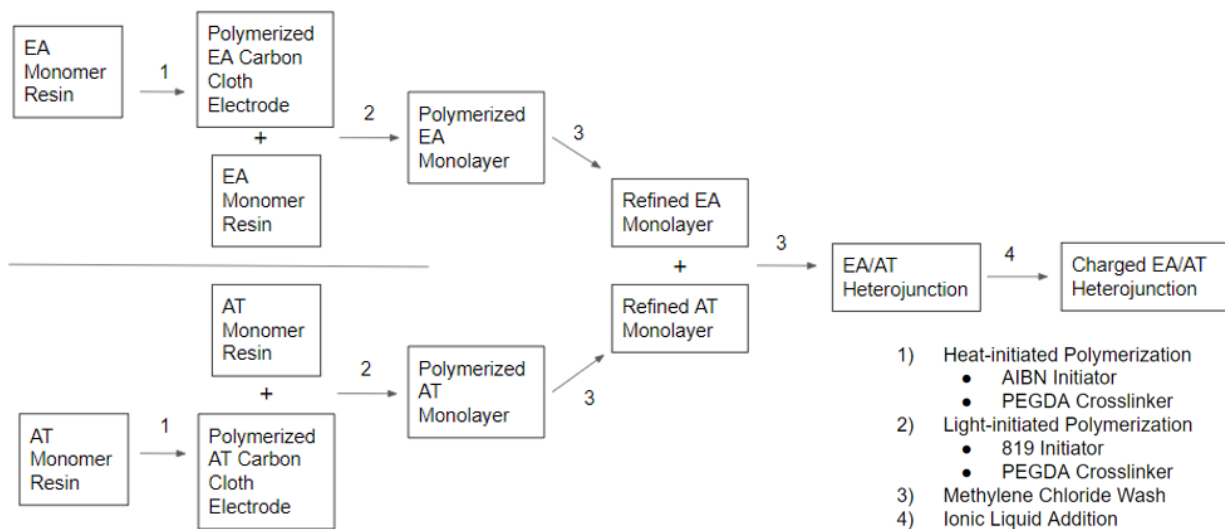


Figure 3.3.2: Heterojunction assembly process with steps (1-4) labeled through legend in bottom right

3.4 Open-circuit Potentials and Rectification Ratio Testing

Once the samples have had time to bathe in salt they were then tested using Gamry Instruments Framework hardware and software for both open-circuit potentials and rectification ratios determined by current-voltage (IV) curves. Potential was induced on each sample at an increasing (and decreasing) rate of 5 mV/s from -1 V to 1 V, for two cumulative cycles per second. Samples were in two states throughout testing: forward and reverse biasing for positive and negative potentials, respectively. Samples were expected to produce behavior resembling that of typical I-V curves with forward bias slopes being a varying magnitude greater than their counterpart reverse bias slopes (Figure 3.4.1).

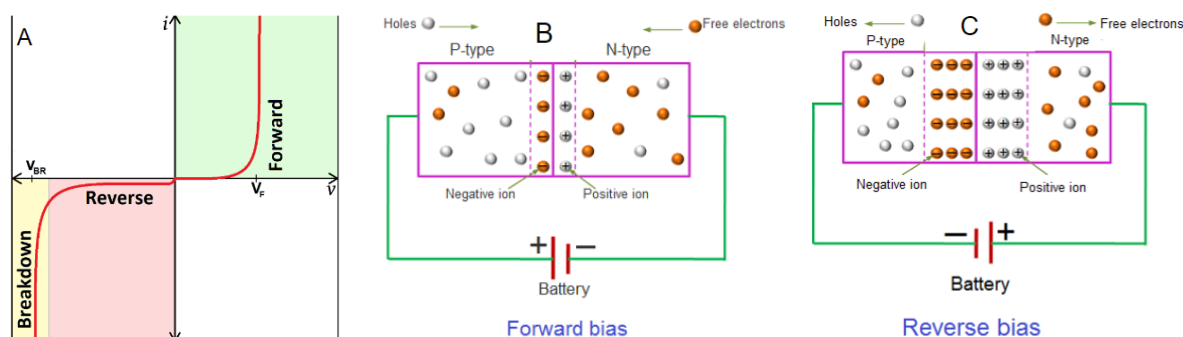


Figure 3.4.1: (A) Semiconductor PIN I-V Curve consisting of forward and reverse biasing, (B)(C) Forward and reverse biasing occurrences for PIN diodes, respectively.

The ratio of these two slopes around the inflection point (V_F in Figure 3.4.1 (A)) reveal the rectification ratio and the intercept of these two projected slopes reveal the threshold voltage, that is the amount of potential difference required for a sample for current to flow through the sample - as indicated by the notable increase in slope that succeeds it. Listed below in Table 3.4.1 are testing specifications that were used for every sample, regardless of ionic liquid concentration.

Table 3.4.1: Cyclic Voltammetry Measurement Specifications

Variable	Value	Units
Electrode Area	0.25	cm ²
Initial Voltage	-1.0	V
Final Volts	1.0	V
Scan Rate	5.0	mV/s
Initial Time Delay	300	s
Cycles	2.0	

Step Size	0.1	mV
Maximum Current	1.0	A

I-V curves were produced in which threshold voltages were not clearly defined by the produced diagrams and so a method in which bias slopes were projected outwards to intersect was implemented so that the intersect and its voltage coordinate could be used as the threshold voltage (Figure 3.4.2). This method was necessary because as alluded to in Figure 3.4.1, the threshold voltage becomes even harder to find with this method when higher concentrations of ionic liquid are induced because the slopes between forward and reverse bias are close to identical. That is why advanced software (Gamry - Table 2.2) was used for this identification.

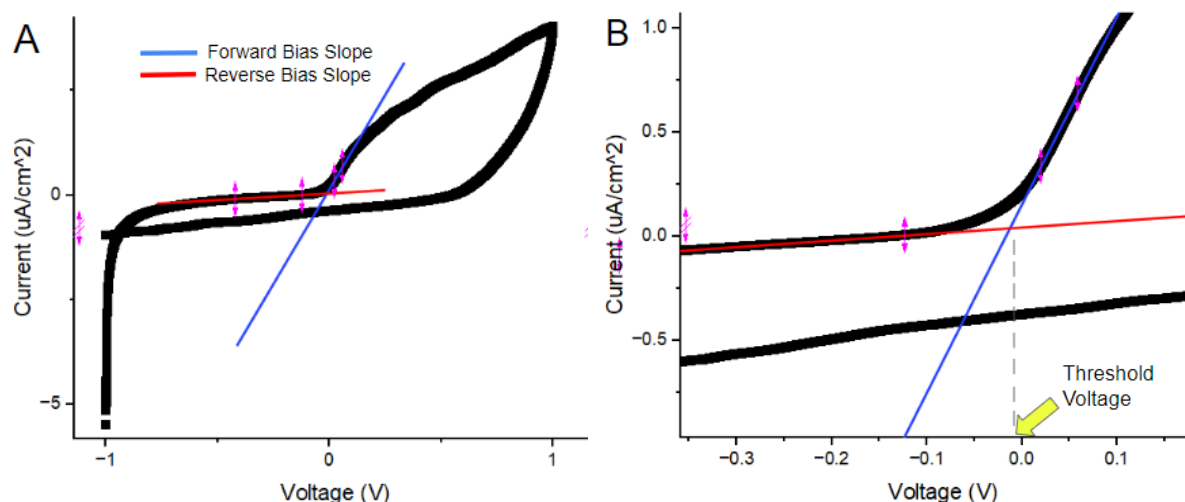


Figure 3.4.2: (A) Bird's eye and (B) zoomed-in view of I-V curve for 1st voltage cycle of 25mM sample (example) showing threshold voltage determination method

3.5 Partitioning Behavior

The amount of ionic liquid that the samples were left to bathe in for 2 days was not the actual amount of ionic liquid that was absorbed into the carbon cloth electrodes and into the resins. To determine the actual concentrations of ionic liquid present in the samples, the samples must be again washed in DCM and measured again for conductivity. Based on the difference in potential, the actual amount of ionic liquid that was present in the samples can be deduced. This change in concentration over multiple samples can lead to the identification of a partitioning coefficient.

4. Results

With the methods described, the following distribution of samples with respect to the amount of ionic liquid theoretically present (Table 4.1).

Table 4.1: Amount of junction samples compiled for each ionic liquid concentration

Treatment Concentration (mM)	# of Samples
0	17
5	3
10	4
15	2
20	2
25	3
35	2
50	2
100	1

Drastically more samples were produced without ionic liquid because as alluded to by the procedure, a singular sample could be tested without salt and then with salt. The actual amount of ionic liquid of each sample was not determined through individual testing involving the partitioning method mentioned but rather with previous experiments that had been performed with the identical junction setup. Using these data, the actual amount of ionic liquid present in the resins were determined (Figure 4.1).

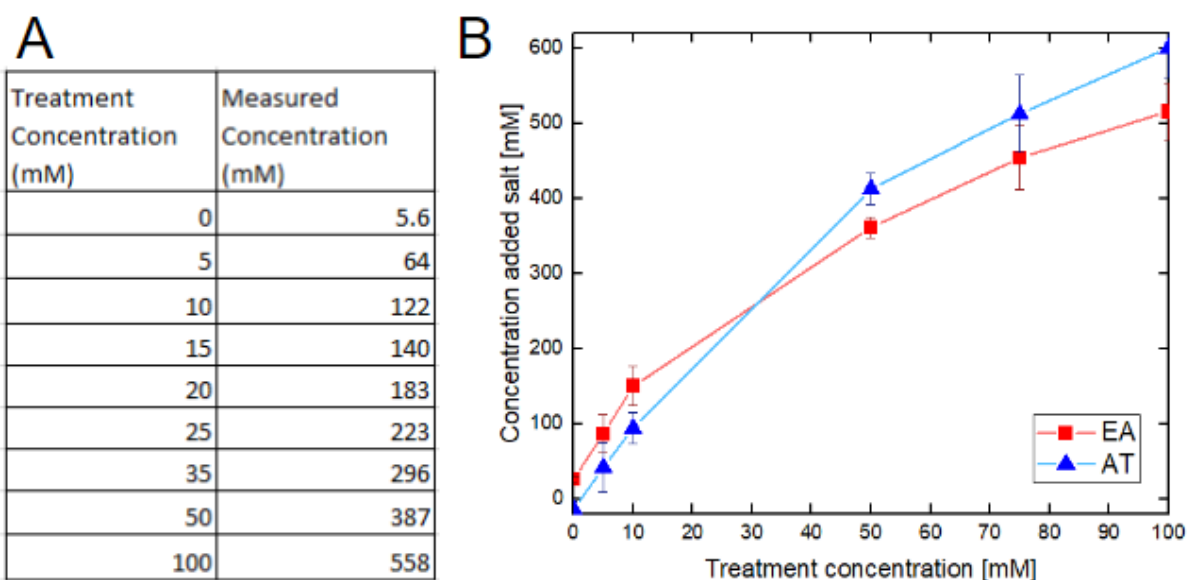


Figure 4.1: (A) Table of concentrations of Ionic liquid induced on heterojunctions converted to amount absorbed by junctions and (B) cited data used to fit curve for translation

Open circuit potentials were first tested through the materials over 300 seconds to see the natural potential of each of the samples, that is voltage without the free ions of the salt moving around. The results are listed below in Figure 4.2:

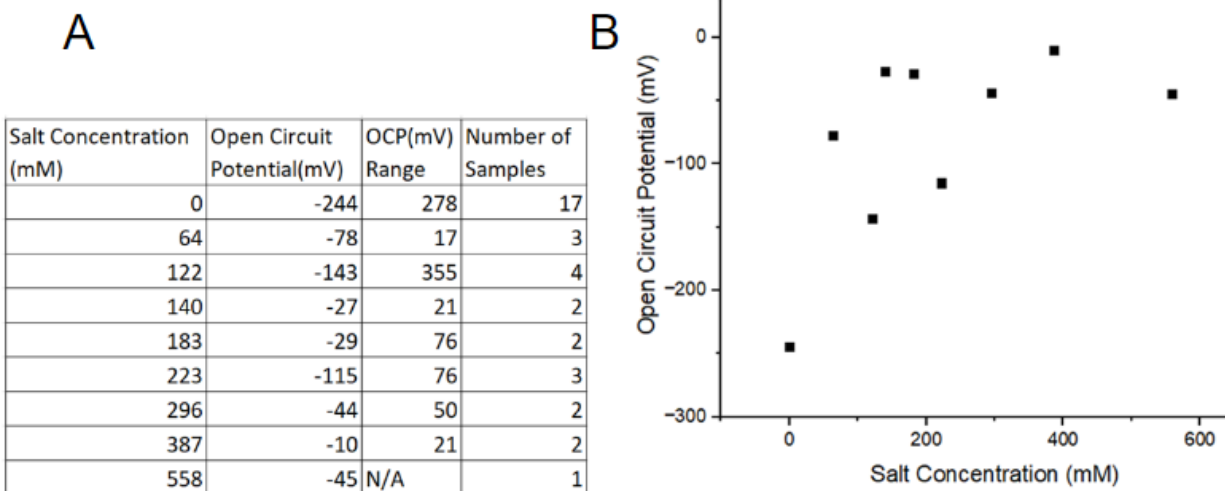


Figure 4.2: (A) Open circuit potentials for all salt concentrations for respective number of samples and (B) plotted results

The data used to produce Figure 4.2 is listed below in appendix A.1. Moving forward, the threshold voltages were measured for each of these samples and the results are shown below in Figure 4.2:

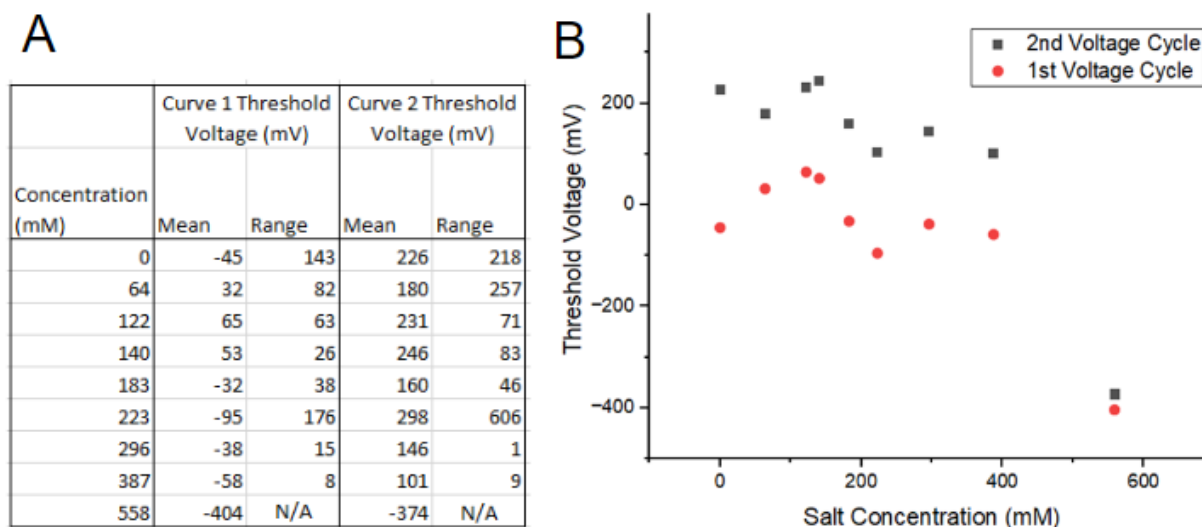


Figure 4.3: (A) Threshold voltages of for each voltage cycle and (B) plotted results

Using the slopes of the forward and reverse biases that were used to produce the intersect of these threshold voltages, the rectification ratios were calculated using Equation 4.1 and the results are shown below in Figure 4.4:

$$\text{Rectification Ratio} = \frac{\text{Forward Bias Slope}}{\text{Reverse Bias Slope}} \quad (4.1)$$

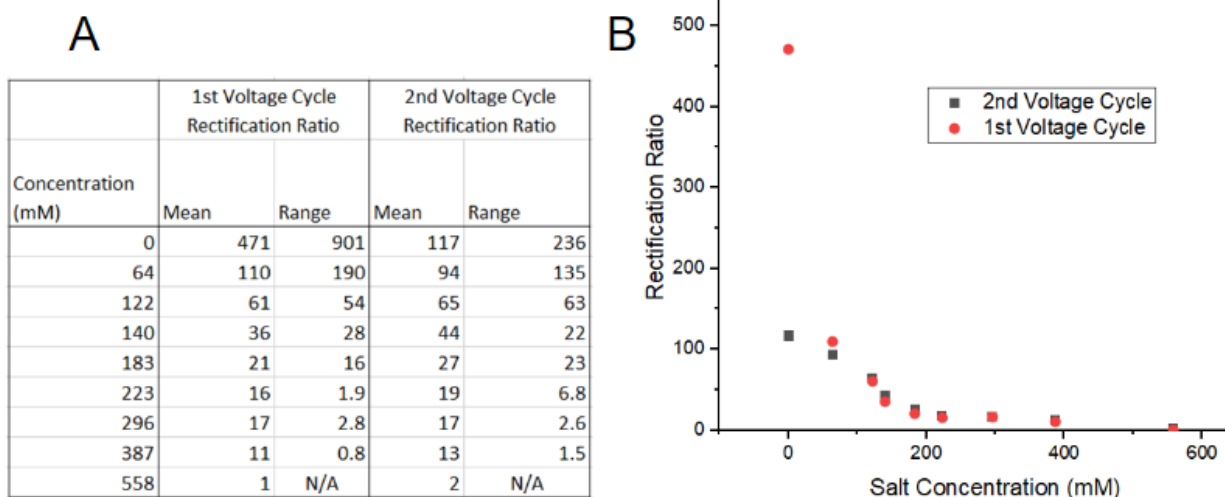


Figure 4.4: (A) 1st and 2nd voltage cycle rectification ratios and (B) plotted results

Lastly, to characterize the hysteresis indicated in Figure 4.4, the amount of change between forward and reverse bias slopes of each voltage cycle was calculated using the following equations (4.2 and 4.3) and are illustrated in Figure 4.5:

$$\text{Forward Bias Change} = \frac{\text{Forward Bias Slope of 2nd Voltage Cycle}}{\text{Forward Bias Slope of 1st Voltage Cycle}} \quad (4.2)$$

$$\text{Reverse Bias Change} = \frac{\text{Reverse Bias Slope of 2nd Voltage Cycle}}{\text{Reverse Bias Slope of 1st Voltage Cycle}} \quad (4.3)$$

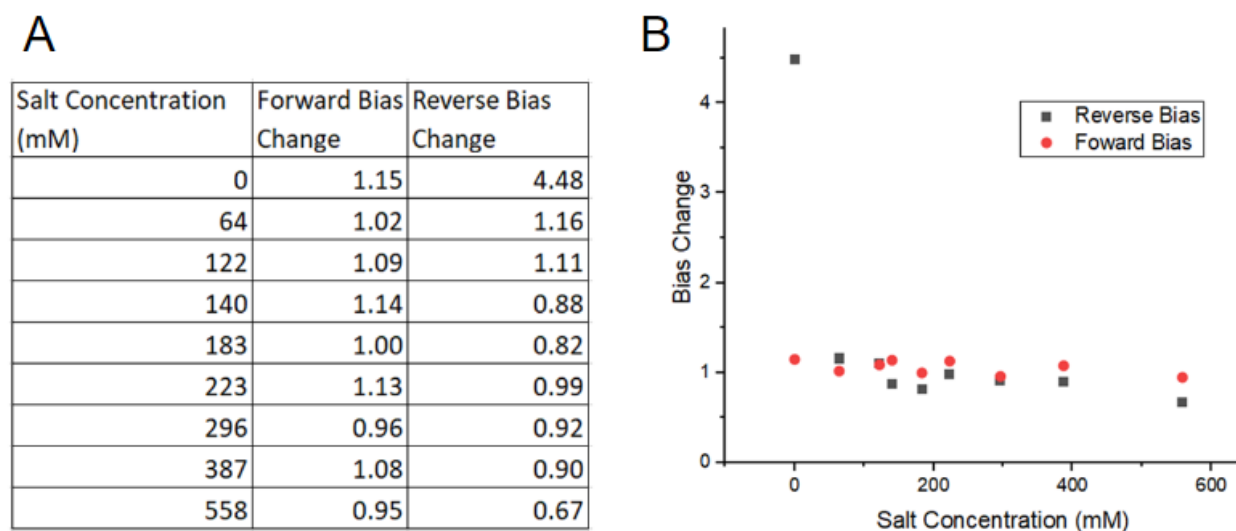


Figure 4.5: (A) Hysteresis trends of both biases for each sample and (B) plotted results

5. Discussion

The first discussion point is the adjustment made between treatment and adsorbed concentration, that is the amount actually present in the junction. Tests were not performed directly on these samples but were rather interpolated from previous data. This data does not cover the exact treatment concentrations and so there is a considerable amount of error pertaining to the medium concentration values (15, 20, 25, and 35mM) (Figure 4.1). The amount of error suspected in doing this was not substantial as the behavior was evidently more sensitive in lower concentration ranges but it is worth mentioning before proceeding to further discussion.

The open circuit potentials shown in Figure 4.2 validate that there is current produced from the presence of added ions which is another way of saying that ions flow. The increasing potential difference across the diodes with increasing salt concentration suggests that the amount of natural ion flow corresponds to the amount of ions present, suggesting that there are no significant steric impedances from the junction's fixed network on the free counterions.

The next result, Figure 4.3, shows the threshold voltages of both voltage cycles for different salt concentrations. The 2nd voltage cycle noticeably produces proportionately higher values in this respect which is indicative of the fact that it becomes increasingly difficult to activate ion flow with greater usage of the junctions. This hysteresis indicates that the ability of the diode to conduct current would gradually decline over time such that the behavior would asymptotically stagger towards minimal performance (conduction). There appears to be no difference in the amount of hysteresis between cycles for different salt concentrations in the smaller ranges - suggesting that ion flow is equally difficult to initiate regardless of the amount of ion flow that is initiated.

To investigate the amount of ion flow through the junctions, the rectification ratios of the forward and reverse bias slopes were investigated for each voltage cycle for each sample and the results are plotted in Figure 4.4. These results show how the forward bias has substantially less prominence with higher salt concentrations of the first cycles than of the second. A higher rectification ratio is indicative of a better conductor and so it is by this that junctions with a lower amount of salt present lose a substantial amount of their performance than junctions with greater amounts of salt for the same amount of cycles run. What is also true is that junctions with a greater amount of salt are limited in maximum performance before any hysteresis occurs.

The hysteresis of these junctions was made most prominent through the results of Figure 4.3 involving the threshold voltages but also through Figure 4.4 involving the rectification ratios. The rectification ratios are a culmination of the reverse and forward bias contributions but it should be explored which of the two steps is the conductance-limiting step. This was done through quantifying the changes from one voltage cycle to another for both the forward and reverse bias slopes. The results of this are in Figure 4.5 and suggest that because of the drastic decrease in reverse bias values, it is the reverse bias contributions or lack thereof that contribute to the evident hysteresis. This, in other words, means that reverse bias fails to move ions across the IDL at the same rate as the forward bias such that the reverse bias is what contributes to the accumulation of ions and thus the gradual failure of the device to conduct current.

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Chemicals

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Appendices

A.1: Open Circuit Potentials, (a) No ionic liquid, (b) ionic liquid

Sample	Voltage (mV)	Measured IL Concentration (mM)	Sample	Voltage (mV)
		64	1	-81.4
			2	-67.4
			3	-84.4
1	-264	122	1	-140
2	-173		2	-363
3	-174		3	-61.7
4	-226		4	-8.2
5	-199	140	1	-37.8
6	-440		2	-16.8
7	-247	183	1	-19.3
8	-291		2	-38.7
9	-245	223	1	-112
10	-255		2	-119
11	-242		3	-42.3
12	-258	296	1	-19.3
13	-162		2	-69.3
14	-265	387	1	-21.1
15	-304		2	0.2
16	-189	558	1	-45.3
17	-224			

(a)

(b)

A.2: Threshold Voltage Data of Heterojunctions at Different Salt Concentrations

Measured IL Concentration(mM)	Sample #	Voltage Cycle	Voltage (mV)
64	1	1st	84
		2nd	267
	2	1st	10
		2nd	10
	3	1st	2
		2nd	263
122	1	1st	71
		2nd	202
	2	1st	74
		2nd	236
	3	1st	89
		2nd	274
	4	1st	26
		2nd	210
140	1	1st	66
		2nd	287
	2	1st	39
		2nd	204
183	1	1st	-13
		2nd	183
	2	1st	-51
		2nd	137
223	1	1st	-165
		2nd	41
	2	1st	-131
		2nd	648
	3	1st	11
		2nd	206
296	1	1st	-30
		2nd	146
	2	1st	-46
		2nd	145
387	1	1st	-62
		2nd	96
	2	1st	-54
		2nd	105
558	1	1st	-404
		2nd	-374